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16. ABSTRACT

In this paper, the authors present generation and waste characteristics information for dioxin wastes and discuss the state of the art for several treatment processes for dioxin wastes that have been proposed to be used instead of landfills for disposing of solid and liquid wastes containing dioxins.

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A Review of

Treatment Alternatives for Dioxin Wastes

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The 1984 Amendments to the Resource Conservation and Recovery Act (RCRA), called the Hazardous and Solid Waste Amendments, (HSWA) direct the EPA to determine if dioxin bearing wastes should be prohibited from landfills. This determination is to be made by November 1986. Barring a determination by the Agency that the land disposal of dioxin wastes does not represent a threat to the environment, or that appropriate alternative treatment technology is not available, a land disposal prohibition would go into effect at that time.[1] The purpose of this paper is to discuss the state of the art for several treatment processes for dioxin wastes that have been proposed to be used instead of land disposal for disposing of solid and liquid wastes containing dioxins.

A dioxin is any of a family of aromatic compounds known chemically as dibenzo-*p*-dioxins. Each of these compounds has as a nucleus a triple ring structure consisting of two benzene rings interconnected to each other through a pair of oxygen atoms. Shown in Figure 1 is the structural formula for the dioxin nucleus.[2]

Most environmental interest in dioxin has centered on chlorinated dioxins in which a chlorine atom occupies one or more of the eight positions on the benzene rings. There are eight chlorinated dioxin homologs and, within these families of homologs, a theoretical possibility of 75 chlorinated dioxin isomers, each with different physical and chemical properties. Most of the interest has been directed toward the isomer 2,3,7,8-TCDD, which is among the most toxic compounds in existence. The compound exists as a colorless crystalline solid at room temperatures and is only sparingly soluble in water and most organic liquids.[3]

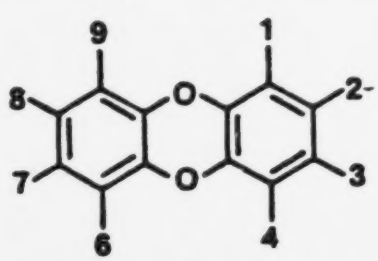

Figure 1. The dioxin nucleus.

Dioxin compounds are apparently not constituents of any normal growing environment, but are formed through manufacturing or combustion processes involving precursor compounds.[2] Dioxins are usually formed in very low yield, i.e. in the ppb and ppt range. Although no definitive studies have determined the exact temperatures of formation, several studies have reported dioxin formation in the range of 180–400°C.[4,5]

Once formed, the dioxin molecule is quite stable. An EPA report on the subject states:

> "Laboratory tests have shown that it is not decomposed by heat or oxidation in a 700°C incinerator, but pure compounds are largely decomposed at 800°C. A recent report states that the nucleus survives intact through incineration up to 1150°C if it is bound to particulate matter. Chlorinated dioxins lose chlorine atoms on exposure to sunlight or to some types of gamma radiation, but the basic dioxin structure is largely unaffected. In comparison with almost any other organic compound, the biological degradation rate of chlorinated dioxins is slow, although measured rates differ widely."[2]

Waste Characterization

Hazardous wastes grouped under the term "dioxin wastes" for the purposes of the RCRA evaluation cover wastes from the production of certain chlorophenols and chlorophenoxy pesticides, manufacturing use of tetra-, penta-, and hexachlorobenzene under alkaline conditions, as well as discarded unused formulations containing tri-, tetra-, or pentachlorophenol and their derivatives.[6] These are listed below, by RCRA classification number.

F020 Wastes (except wastewater and spent carbon from hydrogen chloride purification) from the production or manufacturing use (as a reactant, chemical intermediate, or component in a formulating process) of tri-, or tetrachlorophenol, or of intermediates used to produce their derivatives. (This listing does not include wastes from the production of hexachlorophene from highly purified 2,4,5-trichlorophenol.)

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F021 Wastes (except wastewater and spent carbon from hydrogen chloride purification) from the production or manufacturing use (as a reactant, chemical intermediate, or component in a formulating process) of pentachlorphenol, or of intermediates used to produce its derivatives.

F022 Wastes (except wastewater and spent carbon from hydrogen chloride purification) from the manufacturing use (as a reactant, chemical intermediate, or component in a formulating process) of tetra-, penta-, or hexachlorobenzene under alkaline conditions.

F023 Wastes (except wastewater and spent carbon from hydrogen chloride purification) from the production of materials or equipment previously used for the production or manufacturing use (as a reactant, chemical intermediate, or component in a formulating process) of tri-, and tetrachlorphenols. (This listing does not include wastes from equipment used only for the production or use of hexachlorophene from highly purified 2,4,5-trichlorophenol.)

F026 Wastes (except wastewater and spent carbon from hydrogen chloride purification) from the production of materials on equipment previously used for the manufacturing use (as a reactant, chemical intermediate, or component in a formulating process) of tetra-, penta-, or hexachlorobenzene under alkaline conditions.

F027 Discarded unused formulations containing tri-, tetra-, or pentachlorophenol or discarded unused formulations containing compounds derived from these chlorophenols. (This listing does not include formulations containing hexachlorophene synthesized from pre-purified 2,4,5-trichlorophenol as the sole component.)

F028 Residues resulting from incineration of soil contaminated with EPA hazardous waste Nos. F020, F021, F022, F023, F026, and F027.

These designations include reactor residues, still bottoms, brines, spent filter aids, spent carbon from product purification and sludge from wastewater treatment.[6]

A recent study carried out by EPA's Office of Solid Waste estimates the quantities in Table I for the subject waste streams.[7,8]

Table I. Waste quantity estimates for dioxin bearing wastes (metric tons).

Waste categories	Storage[a]	Current[b]	Future[c]
F020	4300	0	0
F021	0	350	1110
F022	ND[d]	0	0
F023	0	0	0
F026	0	0	0
F027	1000	1000	1000
F028	NA[e]	NA	NA
Total	5300	1350	2100

[a] Storage—wastes that are now in storage awaiting final disposition as a result of previous EPA action. A one time quantity.
[b] Current—quantity of wastes presently generated.
[c] Future—annual quantity of waste expected in near future.
[d] ND—no data.
[e] NA—not applicable.

Current EPA Regulations for Dioxin Wastes

Under existing EPA regulations, dioxin bearing wastes may be stored in tanks, placed in surface impoundments and waste piles, and placed in land treatment units and landfills. However, in addition to meeting RCRA requirements for these storage and disposal processes,[9] the operators of these processes must operate in accord with a management plan for those wastes that is approved by the EPA Administrator. Factors to be considered by the Regional Administrator include:

1. Volume, physical, and chemical characteristics of the wastes, including their potential to migrate through soil or to volatilize or escape into the atmosphere.
2. The alternative properties of underlying and surrounding soils or other materials.
3. The mobilizing properties of other materials codisposed with these wastes.
4. The effectiveness of additional treatment, design, or monitoring techniques.

The Regional Administrator may determine that additional design, operating, and monitoring requirements are necessary for facilities managing dioxin wastes in order to reduce the possibility of migration of these wastes to ground water, surface water, or air so as to protect human health and the environment.[6]

For incineration of dioxin bearing wastes, in addition to the RCRA operation and performance requirements,[10] the incinerator must achieve a destruction and removal efficiency (DRE) of 99.9999 percent for each principal organic hazardous constituent (POHC) designated in its permit. This performance must be demonstrated on POHCs that are more difficult to incinerate than tetra, penta-, and hexachlorodibenzo-*p*-dioxins and dibenzofurans.[6] DRE is determined from the following equation:

$$\text{DRE} = \frac{(W_{in} - W_{out})}{W_{in}} \times 100$$

where: W_{in} = mass feed rate of one POHC in the waste stream feeding the incinerator.
W_{out} = mass emission rate of the same POHC present in exhaust emissions prior to release to the atmosphere.

Of course, the HSWA amendments contain a strong presumption against land disposal. Therefore, one would expect that the Agency's implementation of the HSWA provisions on land restrictions will place primary emphasis on incineration for disposal of dioxin bearing wastes. EPA has also stated that operators of thermal treatment devices must demonstrate that they can meet the performance requirements for incinerators in order to treat dioxin bearing wastes.

Alternative Treatment Technologies for Dioxin Wastes

As indicated in Table II, there are several thermal and nonthermal processes that appear feasible for treating dioxin wastes. While some of these processes have already been tested using dioxin contaminated waste streams, others are either under development or

Table II. Treatment processes for dioxin wastes.

Treatment process	EPA contact
EPA Mobile Incineration System	Frank Freestone[a] (212) 321-6632
Huber Advanced Electric Reactor	Harry Freeman[b] (513) 569-7529
Shirco Infrared System	Harry Freeman
Liquid injection incinerators	Don Oberacker[b] (513) 569-7431
Photolysis	Charles J. Rogers[b] (513) 569-7757
Rotary kiln incineration	Don Oberacker
GA Technologies Circulating Bed Combustor	Harry Freeman
Chemical dechlorination	Garry Howell[b] (513) 569-7756
UV photolysis/APEG chemical detoxification	Charles Rogers
Supercritical fluids	Robert Olexsey[b] (513) 569-7717
White rot fungus	P. R. Sferra[b] (513) 569-7618

[a] Address: Hazardous Waste Engineering Research Laboratory, Edison, New Jersey 08837.
[b] Address: Hazardous Waste Engineering Research Laboratory, Cincinnati, Ohio 45268.

have been tested with other chlorinated waste streams. The processes are presented in order of the availability of data for treating actual dioxin wastes. Those processes which have actually treated dioxin wastes are presented first. Those that appear to have potential but have not actually been used to treat dioxin wastes are presented in subsequent sections. Discussions of each of the processes follow. The names of the EPA contacts in Table II are individuals who are familiar with the processes.

Reference or failure to reference a particular process does not imply that the process is recommended or not recommended by the U.S. Environmental Protection Agency for treating dioxin contaminated wastes. The discussion that follows is a compilation of processes that, from a technical perspective, the authors judge to have potential to treat such wastes. To the extent that test data are available they are presented here. Each specific application of each technology is subject to EPA and state and local regulatory and permitting requirements on a case-by-case basis.

Processes Which Have Been Used to Treat Dioxin Wastes

EPA Mobile Incinerator

EPA's Office of Research and Development has developed a mobile rotary kiln incinerator capable of incinerating hazardous waste at the point of generation. The unit, called the Mobile Incineration System, consists of three major subsystems: 1) combustion and air pollution control equipment mounted on three trailers, 2) continuous flue gas monitoring equipment located in a fourth trailer, and 3) support equipment. Figure 2 describes the Mobile Incineration System.[11]

The incineration system consists of a primary combustion chamber (rotary kiln) where solid or liquid wastes are introduced, volatilized, and partly oxidized and a clean fuel oil-fired secondary combustion chamber (SCC) for completing the combustion process initiated in the kiln. The combustion flue gases pass through a gas cleaning unit designed to collect and remove particulate matter and acid gases prior to discharge through the stack. The initial treatment of the combustion gases is accomplished by water quenching in the quench elbow, which is then followed by particulate removal in a cleanable high efficiency air filter (CHEAF). [The primary function of the elbow is to lower the gas temperature from 1200°C (2200°F) to adiabatic saturation, at approximately 85°C (185°F), and thus reduce the gas volume; some particulate and acid gas removal does occur in the quench elbow.] The final step in the gas treatment process is the removal of acid gas in a cross-flow packed-bed mass-transfer scrubber. The pH of each process water stream is controlled by the addition of sodium carbonate to enhance acid gas removal and to minimize corrosion of the gas cleaning equipment. The prime gas mover for the incineration system is a diesel-powered induced-draft fan that maintains a negative pressure in the entire system so as to prevent the leakage of toxic vapors. The process gas is discharged through a 12-m (40-ft) stack.[12]

In 1983, trial burns were conducted in Edison, New Jersey on RCRA-listed surrogates, including dichlorobenzene, trichlorobenzene, tetrachlorobenzene, Aroclor 1260, and tetrachloromethane (CCl_4). After a solids feed system was installed and tested in December 1984, additional laboratory tests were conducted. Currently, the mobile incinerator is installed at the Denny Farm site near McDowell, Missouri, where "cold" and "hot" tests were conducted using clean soil and soil contaminated with surrogates similar to those employed in the earlier liquid waste tests (CCl_4 and hexachloroethane). Tests using dioxin-contaminated liquid wastes and soil verified the DRE and the effectiveness of the control devices. Interim delisting guidelines were established and analyses were conducted on ash, treated soils, filter materials, and process/quench water to ascertain if the guidelines were attainable.[13]

The dioxin trial burns were successful, with DREs exceeding 99.9999 percent for the POHCs burned. During these tests 3.84 pounds of 2,3,7,8-TCDD, contained in 1750 gallons of liquids and over 40 tons of soil, were

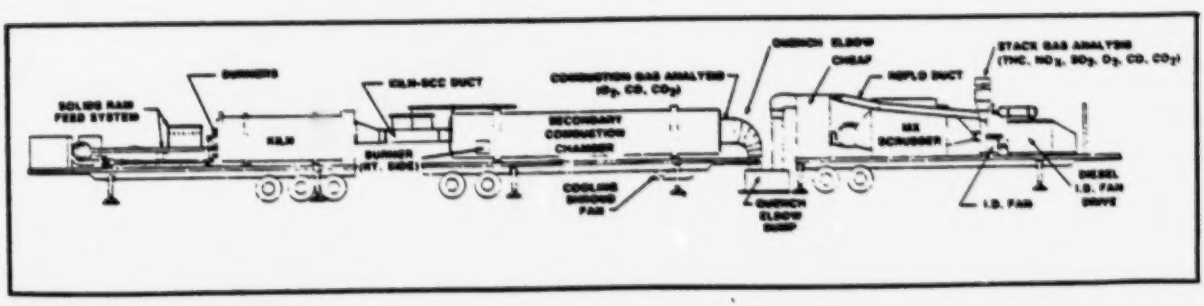

Figure 2. EPA Mobile Incineration System.

destroyed. Particulate emission permit limitations (<180 mg/Nm^3 @ 7% O_2) were achieved in three of four test runs. During the fourth run, particulate emissions exceeded the prescribed limit slightly, possibly due to the accumulation of submicron-sized particles in the air pollution control system. The observed CO emission values (1.3–7.7 ppm) are equivalent to those from the best available incineration technologies and are indicative of very complete combustion (C.E. = 99.993–99.999%).[13]

Finally, the treated soil (ash) and process wastewater from the trial burn were analyzed for a series of specific constituents considered as likely contaminants. The results of these analyses were used to support an application to "delist" residues from a planned larger scale burn of similar wastes.[14]

Advanced Electric Reactor

The Advanced Electric Reactor (AER) is a process designed specifically for on-site detoxification of soils. It is owned by the J. M. Huber Company, Borger, Texas.

The reactor employs a new technology to rapidly heat materials to temperatures between 4000–5000°F using intense thermal radiation in the near infrared region. The reactants, which can be in gaseous, liquid, or solid form, are isolated from the reactor core walls by means of a gaseous blanket formed by flowing nitrogen radially inward through porous graphite core walls. Carbon electrodes are heated and in turn heat the reactor core to incandescence so that heat transfer is accomplished by thermal radiative coupling from the core to the feed materials. Destruction is accomplished by pyrolysis rather than oxidation.[15]

Figure 3 is a simplified process diagram of the AER process. For solid waste treatment, the solid feed stream is introduced at the top of the reactor by means of a metered screw feeder connecting the airtight feed hopper to the reactor. Nitrogen is introduced primarily at two points in the reactor anulus formed by the external containing vessel and the porous graphite core which creates the fluid barrier. The solid feed passes through the reactor where pyrolysis occurs at approximately 4000°F. After leaving the reactor, the product gas and waste solids pass through two post-reactor treatment zones (PRTZ). The first PRTZ is an insulated vessel to provide additional high temperature (in excess of 1100°C, 2000°F) and residence time (5 to 10 seconds) while the second PRTZ is water-cooled. It also provides additional residence time (approximately 10 seconds) but primarily cools the gas to less than 1000°F prior to downstream particulate cleanup.[16,17]

Solids exiting the PRTZ are collected in a solids bin which is sealed to the atmosphere. Additional solids in the product gas are removed by a cyclone and routed back to the solids bin. The product gas then enters a baghouse for fine particle removal followed by an aqueous caustic scrubber for chlorine removal. Any residual organic and chlorine are removed by passing the product gas through activated carbon beds just upstream of the emission stack. The organic, particulate, and chlorine-free product gas composed almost entirely of nitrogen is then emitted to the atmosphere through the process stack.

Among the potential advantages of this process are transportability, extremely high treatment efficiencies (because of the high process temperatures and long residence times), intrinsic safety features (such as the activated carbon beds, electrically driven solids feeder, and large amount of thermal inertia in the reactor), and the ability to detoxify wastes in a pyrolytic atmosphere, thereby minimizing particulate emissions.

Huber has reported several relevant tests that have been carried out over the past two years. A test in the Spring of 1984 to determine the destruction efficiency (DE) and DRE for the process with carbon tetrachloride over a wide range of operating conditions demonstrated greater than six nines (99.9999%) DRE.[15] A September 1983 test on PCB contaminated solids demonstrated better than seven nines DRE and resulted in Huber's facility at Borger, Texas being certified to destroy PCB contaminated solids.[17]

In November of 1984 a mobile version of the Huber unit was used to treat soil containing 2,3,7,8-TCDD in Times Beach, Missouri. Reports of this test state that no 2,3,7,8-TCDD was detected in the treatment soil at detection limits of 0.11 ppb from the 2,3,7,8-TCDD and that no 2,3,7,8-TCDD was detected in the stack gas at detection limits of 0.55 ng/M^3.[18]

The process' most recent test was at a U.S. Navy facility in Mississippi in which some 1000 pounds of soil contaminated with Agent Orange were pyrolyzed. Results for these tests are not yet available.

Shirco Infrared System

The Shirco unit treats waste by metering the waste streams onto a woven metal alloy conveyer belt and passing the waste under infrared heating elements and then burning combustible off-gases in a secondary chamber. The unit currently being tested by Shirco is a portable pilot scale system that is contained in a 45-ft trailer.[19]

The primary chamber is rectangular (2.5 ft × 9 ft × 7 ft) and is lined with multiple layers of ceramic fiber blanket insulation. Infrared energy is provided by heating elements equally spaced along the length of the furnace. The electrically powered heating element

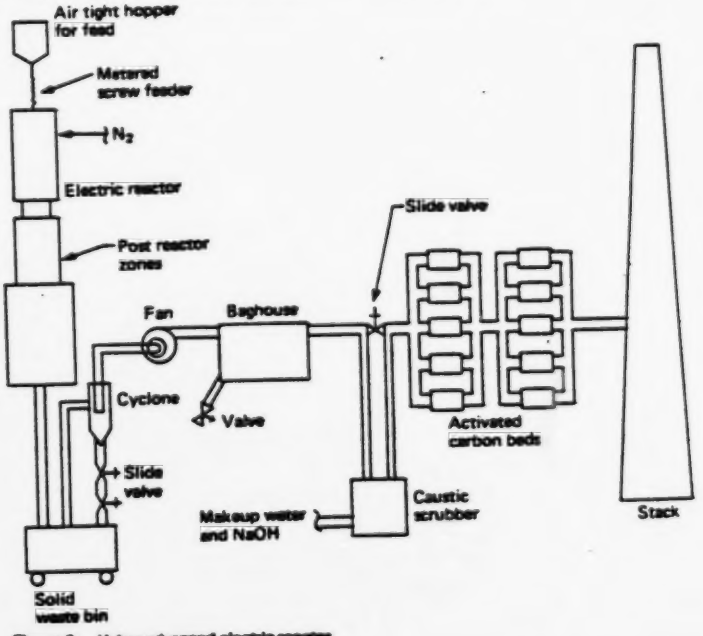

Figure 3. Huber advanced electric reactor.

Table III. Operating conditions for decontamination of dioxin contaminated soil—Shirco system.

Test No.	Solid phase residence time (minutes)	Solid fuel rate (lb/h)	Temperature Zone A (°F)	Temperature Zone B (°F)	Temperature Secondary chamber (°F)
1	30	47.68	1560	1550	2250
2	15	48.12	1490	1490	2235

can provide capabilities of 500–1850°F of process temperature with material residence times variable between 10 and 180 minutes. Oxidizing, reducing, or neutral atmospheres can be provided.[19] A secondary chamber is equipped with a propane burner and is sized to provide gas residence time of up to 2.2 seconds. The process temperature capability is 2300°F. Scrubbers are provided for off-gas cleanup.[19,20]

Shirco has reported successful use of the system to treat municipal and industrial sludges and a simulated creosote pit waste. During the week of July 8, 1985 the unit was used to treat dioxin contaminated soil at Times Beach, Missouri. A summary of the soil decontamination test results is shown in Tables III and IV.[19]

Table IV. Dioxin contaminated soil decontamination test results—Shirco system.

	Test 1	Test 2
Emissions sampling duration (h)	7	2.5
Particulate[a] at 7% O_2 (gr/dscf)	0.0010	0.0002
Gas phase DRE of 2,3,7,8 TCDD	>99.999996[b]	>99.999989
Detection limit (picograms)	14	8.4
Ash analysis for 2,3,7,8 TCDD	ND[c]	ND
Detection limit (ppb)	0.038	0.033

[a] Particulate filter only, without train rinse.
[b] (>) indicates DRE calculations at detection limit.
[c] ND indicates nondetectable.

Liquid Injection Incinerators

A liquid injection system consists of a refractory-lined combustion chamber and a series of atomizing nozzles. It is capable of burning virtually any combustible waste which can be pumped. Wastes to be burned are usually blended in mixing tanks prior to atomization to improve either their pumpability or combustibility, and then are atomized and burned in suspension. The capacity will vary depending upon the energy value of the waste. Typical combustion chamber residence times and temperature ranges are 0.5 to 2 seconds and 1300°F to 3000°F respectively. In addition to being the primary part of a waste combustion system, a liquid injection incinerator is often used as an afterburner to complete the combustion of waste gases following burning in other incinerators such as rotary kilns.

The advantages of liquid injection units include their capability to incinerate a wide range of wastes and their relatively low maintenance costs due to the few moving parts in the system. The primary disadvantage is that they can burn only pumpable liquids, and are susceptible to being shut down because of clogged nozzles. Liquid injection systems are also usually designed to burn specific waste streams and consequently are not often used for multipurpose facilities.

These facilities have been used to destroy a variety of wastes including phenols, PCBs, still and reactor bottoms, solvents, polymer wastes, herbicides, and pesticides. They are not recommended for burning heavy metals, high-moisture content wastes, or materials with high inorganic content.

Liquid injection is a technology in daily use throughout the U.S., both at industrial locations and at central treatment facilities. It is the most commonly used incinerator for hazardous waste destruction,[21] comprising some 64 percent of the market for incinerators.[22]

The incinerators aboard the M/T Vulcanus, an incinerator ship designed to burn chemical wastes on the open ocean, are liquid injection units. The units are vertically mounted with a volume of 131 m^3. Each unit has three rotary cup vortex burners firing into a cylindrical refractory-lined combustion chamber. Each incinerator is capable of burning some 1650 gallons per hour of liquid wastes.[23]

In July–September 1977 the liquid injection incinerators on the Vulcanus were used to destroy Herbicide Orange, an herbicide that contains several chlorinated substances including TCDDs. The reported DE for the TCDD was greater than 99.93 percent, which was the highest DE that could be measured given the detection limits of the TCDD concentration in the exhaust gas.[23] More recent test burns in similar liquid injection units on the Vulcanus II, a sister ship, demonstrated greater than 99.998 DE for the organochlorine CCl_4, $CHCl_3$, and 1,1,2-TCE.[23] The EPA concluded for its evaluation of the 1977 and earlier test burns that oceanic incineration had the potential to be an environmentally acceptable alternative to other means of disposal.[23]

Although incinerator ships are currently available for use, they are neither TSCA or RCRA permitted. However, specific permits will be required by the EPA before any operation in this country can occur.

Photolysis

Photolysis is a process that involves the breakdown of a chemical by light energy. Photolysis studies have shown that chlorinated dioxins may be photolytically degraded in the environment by sunlight.[2]

Polychlorinated dibenzo-*p*-dioxins undergo photolysis rapidly in the presence of hydrogen donors such as alcohols, ethers, hydrocarbons, and natural oils and waxes. The photolytic degradation appears to occur in a stepwise loss of one chlorine atom at a time. Sunlight is effective in activating the reaction and, hence, of all the possible natural detoxification mechanisms, photolysis appears to be the most significant. The ultraviolet wavelengths of light have been shown to be the most effective in causing the degradation reaction.[22]

Under appropriate conditions, certain wavelengths of light convert the more toxic dioxins to less toxic forms by removing halogen substituents. Applications of this principle will, therefore, be limited to decontamination and partial degradation, rather than to complete disposal.

The effectiveness of dioxin photolysis is enhanced by solution of the dioxins in a light-transmitting film, the presence of a hydrogen donor in the solution, and the use of ultraviolet light.[23]

IT Enviroscience, Knoxville, Tennessee, has developed a solvent extraction photolysis process that was applied to dioxin-laden sludge in Verona, Missouri, in 1980. In this process the dioxin was extracted from a sludge using hexane as solvent. The resulting extract was then passed under eight 10-kW lamps to effect the desired reduction.

A report of the work states that "160 gal batches of the waste were run through the destruction process in five

two-week operating periods. Six extractions of the waste reduced the dioxin content from 34 ppm to 0.2 ppm (34 mg/L to 0.2 mg/L). Generally, photolysis reduced the dioxin concentration to less than 100 ppb (0.1 mg/L) with optimum photolysis times of about 20 hours. Air sampling at the single process vent confirmed that no dioxin (less than 0.01 $\mu g/m^3$) was emitted to the atmosphere during operation."[26]

Processes Which Have Potential to Treat Dioxin Wastes

Rotary Kiln Incinerators

The rotary kiln system is the most nearly universal of waste disposal systems. It can be used for a wide variety of solid and sludge waste disposal, and for the incineration of liquid and gaseous wastes.[27]

Rotary kiln incinerators are refractory-lined cylinders mounted with their axes inclined at a slight angle from the horizontal. This type of incinerator has a length-to-diameter ratio between 2 and 10; a rotational speed in the range of 1–5 fpm (measured at kiln periphery); an incline ratio between 1/16 and 1/4 in./ft; an operating temperature upper limit of 3000°F (1650°C), although typical temperatures are lower, and a residence time that can vary from seconds to hours. It can be used to dispose of solids, sludges, liquids, and gases. The speed of rotation may be used to control the residence time and mixing with combustor air.

The primary function of the kiln is to convert, through partial burning and volatilization, solid wastes to gases and ash/residue. The ash is removed and, if found to be free of unacceptable levels of hazardous wastes, is put in a landfill. An afterburner using gaseous or liquid fuels to generate a high-temperature oxidizing environment is almost always required to complete the gas-phase combustion reactions. The afterburner is connected directly to the discharge end of the kiln, where the gases exiting the kiln turn from a nearly horizontal flow path to a vertical flow path upward to the afterburner chamber. The afterburner itself may be horizontally or vertically aligned.[28]

The system is designed so that a negative pressure can be maintained in the kiln in order to minimize emissions at the end seals of the rotating section.

Both the afterburner and kiln are usually equipped with an auxiliary fuel firing system to bring the units up to the desired operating temperatures. The auxiliary fuel system may consist of separate burners for auxiliary fuel, dual-liquid burners designed for combined waste/fuel firing, or single-liquid burners equipped with a premix system. Fuel flow is gradually turned down, and liquid waste flow is initiated after the desired operating temperature is attained.[28]

In rotary kilns, liquid wastes may be fired either at the feed or discharge end of the unit; both cocurrent and countercurrent firing designs are used.

Rotary kilns have the advantages of being able to incinerate a wide variety of liquid and solid wastes, being able to accept drum and bulk containers, and being able to retain waste materials sufficiently long to accomplish very high destruction rates. Rotary kilns are capital intensive and need significant maintenance to maintain seals and refractory.

There are no reported data for the combustion of TCDD in stationary rotary kilns. However, there are several rotary kilns that have been permitted to burn PCB wastes. These kilns have at least the potential for incinerating dioxin waste streams. Three commercial rotary kilns with PCB permits are:

1. ENSCO, El Dorado, Arkansas
2. Rollins, Deer Park, Texas
3. SCA, Chicago, Illinois

Each of these facilities, as part of the trial burns associated with its permit application, reported DREs for PCBs in excess of 99.9999 percent.

Circulating Bed Combustion

Circulating bed combustion technology is a modification of traditional fluidized bed incineration developed by GA Technologies, San Diego, California. Fluidized bed incinerators are vessels, usually some 20–25 ft in diameter and 30 ft high, which contain a bed of inert granular material, usually sand. The bed is kept at a temperature of 840–1560°F. Fluidizing air is passed through a distributing plate below the bed to agitate and heat the granular material. Waste materials and auxiliary fuel are injected radially in small amounts and mixed with the bed material which transfers heat to the waste. The waste in turn combusts and returns energy to the bed. Figure 4 describes the circulating bed process.[29]

Circulating bed technology extends fluidized bed technology by increased turbulence and throughput per unit area. The incinerator uses high air velocity and circulating solids to create a highly turbulent combustion zone. Because of the high air velocity, solids are entrained and combustion takes place along the entire height of the combustion section. Solids are separated from off-gases by an integral cyclone and returned to the combustion zone through a nonmechanical seal. Temperatures are uniform with ±5°F variance throughout this loop. This uniform temperature and high solids turbulence avoids the ash slagging encountered in other types of incinerators. Turbulence is a prime factor in the zone. Nitrogen oxide (NO_x) and carbon monoxide (CO) emissions are reported to be well controlled by the good mixing, relatively low temperatures (1450–1500°F), and staged combustion achieved by injecting secondary air at higher locations in the combustor.[29]

The unit is designed to control pollution by the efficient combustion/des-

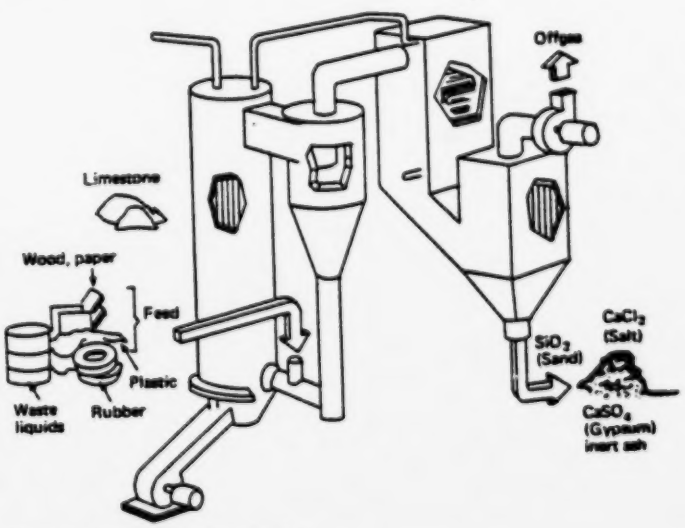

Figure 4. Circulating bed combustion.

Table V. PCB trial burn results—GA Technologies Circulating Combustor.

Parameter	Test 1	Test 2	Test 3
Soil feed rate, lb/h	327.5	411.5	323.8
Total soil fed, lb	1,310	1,646	1,295
PCB concentration in feed, ppm	11,000	12,000	9 800
Combustion efficiency, %	99.94	99.95	99.97
Residence time, sec	1.18	1.18	1.22
Destruction temperature, °F	1,805	1,805	1,795
DRE, %	>99.9999	>99.9999	>99.9999
Particulate concentration			
Dry, gr/dscf	N/R	0.0425	0.0024
Wet, gr/acf	N/R	0.0227	0.0013

truction of principal organic hazardous constituents (POHCs); efficient retention of halogens, phosphates, and sulfur; and collection of particulate matter. Circulating bed combustion burns solids, liquids, and sludges in the presence of dry limestone to control acid gases without wet scrubbers. Since most particles circulate until combustion is complete, ash volume is minimized. Effluent from the circulating bed incinerator consists of dry ash. Upset response in the circulating bed is to slump the bed, thus retaining pollutants in the stagnant bed of limestone and ash. Experience in full-scale commercial plants shows that the slumped bed is easily and quickly brought back to turbulent circulation.[29]

Because of the fines recycle system, circulating bed incinerators use fewer mechanical components in the system. The developer claims that this results in a more efficient, less costly unit than the conventional fluidized bed combustor.

The high combustion efficiency and good heat transfer in the circulating bed incinerator allows heat to be recovered from low-grade fuels and wastes. The combustion chamber itself is of "water-wall" construction, so that cooling tubes need not be located in the direct path of solids. A flow diagram for a circulating bed combustor is shown in Figure 4.

A trial burn of soils contaminated with PCB was carried out in the GA Technologies pilot scale 16-in. diameter circulating bed combustor on May 7, 1985. The goal of the tests was to demonstrate that the unit could decontaminate soil contaminated with 10,000 ppm PCB. The material used for the tests was soil spiked with PCB.

Results for these tests are presented in Table V. Dioxins and furans are possible products of incomplete combustion. In the tests ppb quantities of chlorinated dioxins were found in the feed soils only. No indication of the compounds was found in any byproduct of the combustion process.[30]

Chemical Dechlorination

Dechlorination processes use chemical reagents to remove chlorine from chlorinated molecules, to break apart chlorinated molecules, or to change the molecular structure of the molecules. Metallic sodium is typically the reagent used to strip the chlorine away from constituents to form sodium chloride. Other proprietary reagents are often used in conjunction with metallic sodium to further treat the dechlorinated constituents. The majority of the dechlorination research has been aimed at the detoxification of PCBs. This research is applicable to many chlorinated organic molecules, including 2,3,7,8-tetrachlorodibenzo-*p*-dioxin.

Several companies and research institutions have dechlorination processes. Three of the dechlorination technologies include the Acurex process, PPM process, and Sunohio PCBX process. These processes have been found effective in reducing the toxicity of PCBs and other chlorinated organics.

The Acurex process uses a sodium reagent with a proprietary constituent. The treatment stream is filtered prior to further treatment. After filtration, the stream is transferred to a reaction tank where it is mixed with the sodium/proprietary constituent mixture. The products of this reaction are a sodium chloride stream and another nontoxic effluent.

The Sunohio PCBX process, unlike the Acurex process is a continuous treatment operation. This process uses a proprietary reagent to convert the PCB molecules to metal chlorides and polyphenyl compounds.

The PPM process uses a proprietary sodium reagent to dechlorinate organic molecules. This process is a batch process. A solid polymer is generated from the reaction and this substance, although regulated, can be more easily disposed of than the chlorinated organics.

The above described processes may be applicable to many chlorinated organics, such as PCBs, dioxins, solvents, and pesticides.[31]

The Acurex process has been tested for removal of chlorinated waste from soils. A commercial unit designed to treat soil is in the early stages of development. In transformer oil, 2,3,7,8-TCDD has been reduced from 200–400 ppt to 40 ± 20 ppt using the Acurex process. This system cannot be used on aqueous streams.[31]

The Sunohio PCBX process has reduced PCB contaminated transformer oil from 225 ppm to 1 ppm in one pass through the system. It is believed that, by passing the oil through the system three times, PCBs can be reduced from 3000 ppm to less than 2 ppm. This process was used at a number of sites, including Maxwell Laboratories in San Diego, where 163,000 gallons of PCB contaminated oil were processed, and Chevron in El Segundo, California, where a total of 5250 gallons of oil initially containing 420–1500 ppm PCBs were processed.[31,32]

The PPM process has reduced the PCB concentration in contaminated oil from 200 ppm to below detection levels. As with all of the sodium processes, this process cannot be used on aqueous wastes.[31]

As part of its program to identify and encourage new and effective processes for treating dioxin wastes, EPA's Hazardous Waste Engineering Research Laboratory (HWERL) has supported research with the use of alkaline polyethylene glycols (APEGs) to destroy dioxins. The ultimate objective of the APEG program is to develop reliable and cost-effective techniques for the destruction and/or detoxification of toxic halogenated organics, including 2,3,7,8-TCDD. The specific objective of current research is to determine the degree of effectiveness of APEG reagents singly and in conjunction with UV irradiation.[14]

Laboratory experiments using 1,2,3,4-TCDD have demonstrated the ability of APEG reagents to chemically reduce concentrations of that isomer in wastes. While laboratory studies have investigated in situ applications of APEG to contaminated soils, recent research has focused on slurry application of the reagent to dioxin contaminated wastes and soils. The slurry approach incorporates reagent recovery and recycle.

While the chemical dechlorination processes are at least theoretically applicable to dioxin waste streams, more research and testing is required before adequate technical comparisons can be drawn between the capabilities of the thermal destruction processes and the chemical dechlorination processes. The fact that the sodium based processes cannot be applied to aqueous waste streams will limit the applicability of these systems.

Supercritical Fluids

Some supercritical fluids, i.e. liquids or gases at or above their critical tem-

perature and pressures, have been found to be excellent solvents for organic wastes.

In the supercritical waste process developed by the MODAR Company, Natick, Massachusetts, an aqueous waste stream is subjected to temperatures and pressures above the critical point of water, i.e., that point at which the densities of the liquid and vapor phase are identical. (For water the critical point is 714°F and 219 atmospheres.) In this supercritical region water exhibits unusual properties that enhance its capability as a waste destruction medium. Because oxygen is completely miscible with supercritical water, the oxidation rate for organics is greatly enhanced. Also, inorganics are practically insoluble in supercritical water. This factor should allow the inorganics to be removed from the waste streams. The ideal result is that organics are oxidized rapidly and the resultant stream is virtually free of inorganics.[14,15]

A brief summary of this concept, described in Figure 5 is:

1. Waste is slurried with make-up water to provide a mixture of 5 percent organics. The mixture is heated using previously processed supercritical water and then pressurized.
2. Air or oxygen is pressurized and mixed with the feed. Organics are oxidized in a rapid reaction. (Reaction time is less than 1 minute.) For a feed rate of 5 weight percent organics, the heat of combustion is sufficient to raise the oxidizer effluent to 930°F.
3. The effluent from the oxidizer is fed to a salt separator where inorganics are precipitated out.
4. Waste heat from the process can be reclaimed to provide sufficient energy for power generation and high pressure steam.

Bench scale experiments with the supercritical water process have yielded organic carbon destruction efficiencies of from 99.970 to 99.996 percent for a range of chlorinated organic compounds. For PCBs in transformer oil and a methyl ethyl ketone matrix, average organic carbon destruction efficiency was 99.991 percent.[33]

Another process, using supercritical CO_2, has been proposed to extract PCBs from soil particles.[34] In this process, which is still in laboratory development, over 90 percent of PCB contamination in soil was extracted in under one minute. Work is continuing on this medium of treatment.

Given the low levels of TCDD contamination normally found in dioxin contaminated wastes, it is unlikely that supercritical CO_2 will prove to be viable for TCDD waste treatment. If supercritical water can demonstrate specific TCDD compound destruction efficiencies in the range of those for organic carbon in the previous laboratory work, the supercritical water process may have potential, particularly for highly aqueous dioxin contaminated wastes or leachates that present a problem for the sodium based dechlorination processes.

White Rot Fungus

Through its biodegradation research program, EPA is supporting work to identify, develop, and test microorganisms capable of degrading highly toxic and refractory organohalide pollutants, including 2,3,7,8-TCDD.

Although research has not yet identified organisms considered capable of treating 2,3,7,8-TCDD, it has identified an organism, the white rot fungus, *Phanerochaete chrysosporium*, that appears very promising. The fungus secretes a unique hydrogen peroxide-dependent oxidant capable of degrading lignin. Recent reports on this research indicate that the substrate is not only effective in degrading lignin, but also is effective in degrading organo-halides such as lindane, DDT, 4,5,6-trichlorophenol and 2,4,6 trichlorophenol.[35]

It is proposed that the fungus may prove to be suited for use in biotreatment processes for the degradation of refractory organic pollutants. To date, work with this primary alternative has been confined to the laboratory. EPA's HWERL is planning to test the enzyme system at several contaminated sites in the future.[14]

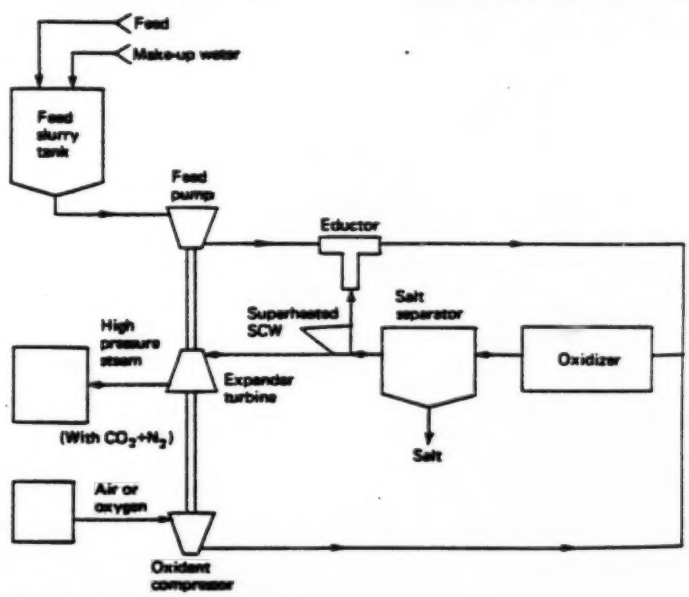

Figure 5. Supercritical water process.

Summary

This article has identified and discussed many alternative technology options for treating dioxin wastes. As the U.S. continues to move away from land disposal toward more acceptable techniques for managing hazardous wastes, processes such as the ones discussed will become more common as waste management options. While many of the processes described here may now appear to be expensive or exotic, as EPA moves to implement the landfill restrictions imposed by Congress, these processes may assume more practicality. Most certainly, the adoption of advanced technologies such as those described here will measurably improve the quality of the environment.

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HAZARDOUS WASTE NEWS

Ebasco Wins EPA Hazardous Waste Contract

Ebasco Services Incorporated, an ENSERCH engineering and construction company headquartered in New York, has been awarded a $200 million contract from the U.S. Environmental Protection Agency to supervise and manage National Priority List hazardous waste sites throughout the Eastern Region of the United States.

The Remedial Engineering Management contract, known within the agency as the REM III Project, is a five-year program to establish the corrective treatment and cleanup schemes for more than 100 National Priority List Hazardous waste sites throughout the Eastern Region. Ebasco will manage this contract from its Washington, D.C. REM III Project Management Office and satellite offices in Boston, New York, Philadelphia, and Atlanta.

The terms of the REM III contract call for Ebasco to provide overall program management for EPA Regions I, II, III and IV, which basically comprise the eastern half of the country. It will also have direct responsibility for sites in Region II (New Jersey, New York and Puerto Rico) and backup responsibility in the other three regions. The contract calls for remedial investigations at NPL sites, feasibility studies, analytical laboratory services, design and consulting engineering, and construction management services.

William Wallace III, Ebasco Chairman and Chief Executive Officer praised the team responsible for winning the contract, and noted that REM III will have a significant impact on the firm. "REM III is important to us not only because of its size as a $200 million contract, but also because it gives us a significant presence in what is a growing market for us. It will strengthen our longstanding commitment to protect the environment through the balanced application of proven and emerging technologies," Wallace said.

Acting as the principal member, Ebasco has assembled a team of firms which includes NUS Corporation of Gaithersburg, Maryland; E.C. Jordan Company of Portland, Maine; Environmental Science & Engineering Company of Gainesville, Florida; and ICF, Inc. of Washington, D.C. The Ebasco team provides EPA with qualified and experienced management and technical resources that possess regional sensitivity, experience with hazardous waste site remediation, and other institutional and technical matters. Under the contract, Ebasco will receive the full $200 million upon EPA's exer-